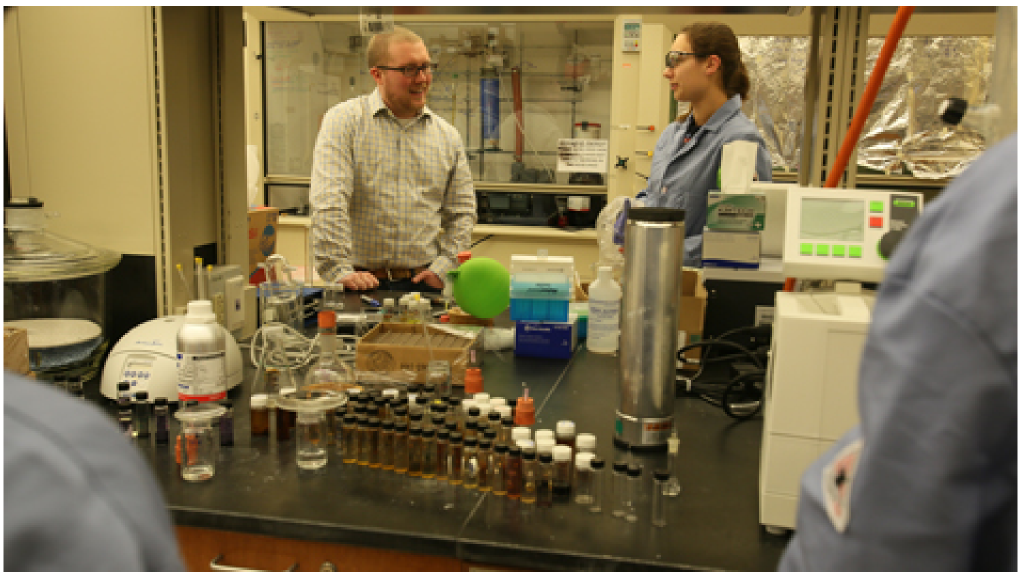
# Is artificial photosynthesis the next big thing in alternative energy?

January 29 2015, by Alla Herman



Assistant Professor of Chemistry William McNamara discusses progress on artificial photosynthesis with students in his lab, including Catherine Wise '15. Each student is investigating an abundant-earth catalyst to facilitate a device to turn sunlight into hydrogen gas. Credit: Stephen Salpukas

William & Mary chemist William McNamara is taking a "bio-inspired" approach to the world's energy crisis by turning to nature's very own chemical power plant: photosynthesis.

McNamara and his students are working on creating cleaner, more efficient and more cost-effective ways to harvest energy by mimicking the way plants use sunlight to create their own energy.

"If you look outside there are all these organisms that are doing exactly what we want to do. Plants take in sunlight, and they're able to make a fuel out of it in the form of sugars that they use to power themselves," McNamara said.

One of the most effective resources for harvesting "greener" energy uses sunlight as a natural energy source. Solar cells absorb sunlight to generate electricity, which can be used to power devices or stored in batteries.

Solar cells are a greener way of harvesting energy, but some major limitations inhibit the technology from replacing traditional energy sources. According to McNamara, one limitation is that when the sun is not shining, no electricity is being harvested and stored in batteries. This means only a certain amount of energy can be collected. In the dark, you are on battery power and experience a loss of efficiency. He added that solar cells also are very expensive and so traditional solar technology is not as widespread as it could be.

"These things are often driven economically as to what we use as a technology. It's not yet feasible for us to be using solar everything," McNamara said. "The pricing isn't as competitive as oil right now. It would take an overhauling of our infrastructure to make it more usable."

McNamara, assistant professor of chemistry, was inspired by the thought that nature had already created superior ways to use sunlight. His "bio-inspired" approach begins with sunlight and ends with hydrogen gas that can be used as a fuel.

Basically, he explained, the process runs a bit of solar power through water and a catalyst reduces protons to hydrogen gas, leaving some leftover water.

"If your catalyst is really efficient, you would produce more hydrogen gas then you could possibly use in an evening when the sun is not shining," McNamara said. "And there is a low carbon footprint."

Understanding of the reduction reaction necessary for reducing protons to hydrogen gas is well established, but McNamara says the current state of the science makes a marketable artificial photosynthesis device too expensive. The chemistry requires metallic catalysts and current researchers have found that some of the best and most efficient artificial-photosynthesis catalysts are made from expensive metals such as platinum and rhodium.

McNamara and his team of students are turning, once again, to nature's own solution to create a catalyst by using earth-abundant metals, such as iron. This would change the scale on which solar energy could be used, as metals like iron are very cheap. Each student is testing a different catalyst to see which combinations of earth-abundant metals produce hydrogen most efficiently. McNamara's interest in using earth-abundant metals to make catalysts comes from research into the chemistry of photosynthesis and other natural processes.

"Your blood hemoglobin doesn't use a precious metal. It uses iron because we've evolved with a lot of iron around us. Photosynthesis uses manganese because there's a lot of manganese on Earth," McNamara said. "We're trying to develop a catalyst to make hydrogen from water using earth-abundant, inexpensive iron. Iron is the most abundant transition metal on this planet, so it's obviously very inexpensive. It's everywhere."

Kathryn Mayer '15 joined McNamara's lab as a sophomore. Majoring in chemistry and pursuing a minor in environmental science, she is applying to graduate schools and hopes to become an atmospheric chemist, studying the stew of compounds that infiltrate the air we breathe.

In the meantime, Mayer works on artificial photosynthesis. She is one of three student co-authors on McNamara's paper "Hydrogen Evolution Catalyzed by an Iron Polypyridyl Complex in Aqueous Solutions," along with two 2014 graduates, Gannon Connor and Connor Tribble. The paper, published in *Inorganic Chemistry*, outlines the group's progress in iron-catalyst solutions to artificial photosynthesis.

McNamara has his students working with a number of abundant metals, including nickel and cobalt, but he says he likes the lab to concentrate on iron catalysts. Each metal is tested with one or more ligands, molecules that bind to the metal by sharing electrons. The ligands act as a kind of electrochemical volume knob.

"What I like about this approach is that I can physically tune the ligands to get them to do the reaction at a specific potential," McNamara said. "The potential is important because if the potential is very negative, it's going to require a lot of energy to do that reaction."

The lab is searching for the ideal metal-ligand complex for artificial photosynthesis, what McNamara calls "the sweet spot of efficiency and activity." In practice, that means a combination that will provide a long-lasting, stable reaction, allowing construction of a practical device that will go on splitting water into hydrogen and oxygen for months or years without requiring too much maintenance.

There are a lot of possible metal-ligand combinations, which is why McNamara has his students investigating as many likely pairs as possible. Mayer, for example, has been working on the iron-polypryridyl complex featured in the Inorganic Chemistry paper since the summer before her junior year.

"What's interesting about it is that iron complexes usually don't work in water, but this one does," she said.

Mayer explained that each investigation begins with synthesizing the ligand. In her case, the synthesis was fairly straightforward, although some ligand synthesis requires more than usual care.

"There are a couple of chemicals that are toxic in the air, so you have to work with them in the hood, using small amounts at a time," she explained. "Some of the chemicals are pyrophoric—they combust on contact with the air. We use very tiny amounts and we're very cautious."

Once a ligand is synthesized, the experimenters can begin electrochemistry experiments. The catalyst goes into a small cell with a source of protons—usually an acid—and solvent, then the chemists apply voltage.

"We're looking at electrons being transferred in the chemical process," Mayer said. "You analyze the data and you can tell what's happening at a very fundamental level."

Once the fundamental electrochemistry is understood, it's time for the experiment to see the light of day—but not literally. Even though the idea of artificial photosynthesis is to use natural sunlight, the lab requires the control offered by an arc lamp.

"After we understand the catalytic properties of the complex through the electrochemical experiments, we move on to photochemical studies. This is where it's more like real artificial photosynthesis. The catalyst is paired with a chromophore. It's like chlorophyll in plants—it's our synthetic equivalent to that. Our iron complex works well with fluorescein, which is a fairly cheap, nontoxic molecule. That's nice. We put that in a test tube together. It's sealed and we shine a light on it and we can measure hydrogen production."

McNamara's work was funded by a Virginia Space Grant Consortium New Investigator Award and also through a Multi-Investigator Cottrell College Science Award from the Research Corporation, with Assistant Professor of Chemistry Kristin Wustholz. The lab has a second paper—with student co-authors—under review at Inorganic Chemistry, and McNamara is writing a third.

The use of catalysts based on common metals could be the key to a more affordable, cleaner energy source. McNamara explained that the use of highly available earth-abundant metals would provide an alternative for developing countries still relying on coal due to its low cost and accessibility.

"It's really hard to convince people in the developing world to use something that's very expensive to make energy when they are sitting on a ton of coal," McNamara said.

According to McNamara, one added benefit of using this method is that one of the byproducts of the reaction is clean drinking water.

"In a developing country, take dirty water from a river and split it to give you hydrogen, burn that and then distill off clean water that you can drink," McNamara said.

This technology could also serve many other purposes. McNamara explained that one such purpose could be allowing the space station to generate its own fuel using sunlight. Not only would it save space and resources, but it would also allow dirty water to be recycled in space.

"You don't want to be hauling up gallons of gasoline to store in tight quarters. This would allow for the space station to generate its own fuel and produce water on the side," McNamara said.

Although McNamara's research offers important solutions to some of the world's most pressing energy issues, he stressed that the most important thing is that we keep finding ways to improve how we harvest and use energy, no matter what the source.

"It is critically important that we research all areas of renewable energy. From a speed standpoint, maybe wind will come along faster than solar," McNamara said. "As long as we keep working on it."

**More information:** "Hydrogen Evolution Catalyzed by an Iron Polypyridyl Complex in Aqueous Solutions." *Inorg. Chem.*, 2014, 53 (11), pp 5408–5410 DOI: 10.1021/ic500069c

Provided by The College of William & Mary